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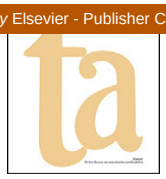

Enthalpy of mixing of liquid systems for lead free soldering: Ni–Sb–Sn system

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ABSTRACT

The partial and integral enthalpies of mixing of liquid ternary Ni–Sb–Sn alloys were determined along five sections x_{Sb}/x_{Sn} = 3:1, x_{Sb}/x_{Sn} = 1:1, x_{Sb}/x_{Sn} = 1:3, x_{Ni}/x_{Sn} = 1:4, and x_{Ni}/x_{Sb} = 1:4 at 1000 °C in a large compositional range using drop calorimetry techniques. The mixing enthalpy of Ni–Sb alloys was determined at the same temperature and described by a Redlich–Kister polynomial. The other binary data were carefully evaluated from literature values. Our measured ternary data were fitted on the basis of an extended Redlich–Kister–Muggianu model for substitutional solutions. Additionally, a comparison of these results to the extrapolation model of Toop is given. The entire ternary system shows exothermic values of $\Delta_{mix}H$ ranging from approx. −1300 J/mol, the minimum in the Sb–Sn binary system down to approx. −24,500 J/mol towards Ni–Sb. No significant ternary interaction could be deduced from our data.

1. Introduction

At the first of July 2006, the ROHS Directive of the European Union ("Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment 2002/95/EC" [1]) has come into force. Due to this directive the use of lead is prohibited in electronic products, however, with a number of exemptions due to reliability issues [2]. Similar regulations are active or impending in various other parts of the world. Over the last decade, due to this global demand for Pb-free soldering, many alloy candidates for replacement of hitherto used Pb–Sn solders have been developed. Among all Pb-free solders, Sn-based alloys are most widely used in electronics. Sn is a rather easily available, inexpensive and nontoxic low melting element that forms alloys and compounds with many metals of importance in electronic applications.

While for low temperature soft soldering suitable materials have been found, e.g. Sn–Ag–Cu and Sn–Cu–Ni, no convenient alloy has so far been found for high-temperature soft soldering (melting temperature ≥230 °C). At the moment Sn–Zn, Sn–Sb and Sn–Au containing solders are promising candidates, while Cu and Ni may be used as additions and as contact materials as well. In general, systems of the type solder + substrate are characterized by huge differences in the melting points of the pure components. The high melting areas cannot be investigated experimentally at the temperatures relevant for soldering, i.e. 200–300 °C, because diffusion is slow and thermodynamic equilibrium will not be reached in reasonable time. Furthermore, multiple component systems of four or more metals cannot be explored with experimental methods only. Therefore a combination of experiments and thermodynamic modeling is needed. Methods like CALPHAD strongly depend on experimental data, especially on thermochemical information like Gibbs energy or enthalpy. Thus the subject of the present study is the experimental investigation of the enthalpy of mixing of liquid alloys in the ternary Ni–Sb–Sn system.

2. Literature review

In the literature we have found a number of results of calorimetric measurements in the binary systems Ni–Sb, Ni–Sn and Sb–Sn at various temperatures. They are summarized as follows:

2.1. The Ni–Sb binary system

Several authors have measured enthalpies of formation, activities and related data of solid Ni–Sb alloys, but no data are available for the liquid Ni–Sb system. Zhang et.al. [3] have presented a brief literature review and they have estimated the interaction parameters ^{v}L of the Gibbs Energy for the liquid phase using the CALPHAD method. The calculated enthalpy values for T = 0 K yield to a curve with a minimum at 54 at.% Ni and $\Delta_{mix}H$ = −18,500 J/mol. Another thermodynamic assessment was published by Cao et al. [4] showing much more negative values of down to −33,000 J/mol for $\Delta_{mix}H$. However, this calculation was based on a misinterpretation of experimental values of Korber and Oelson [5]. The final state of the Ni–Sb mixture was solid and thus the given enthalpies of

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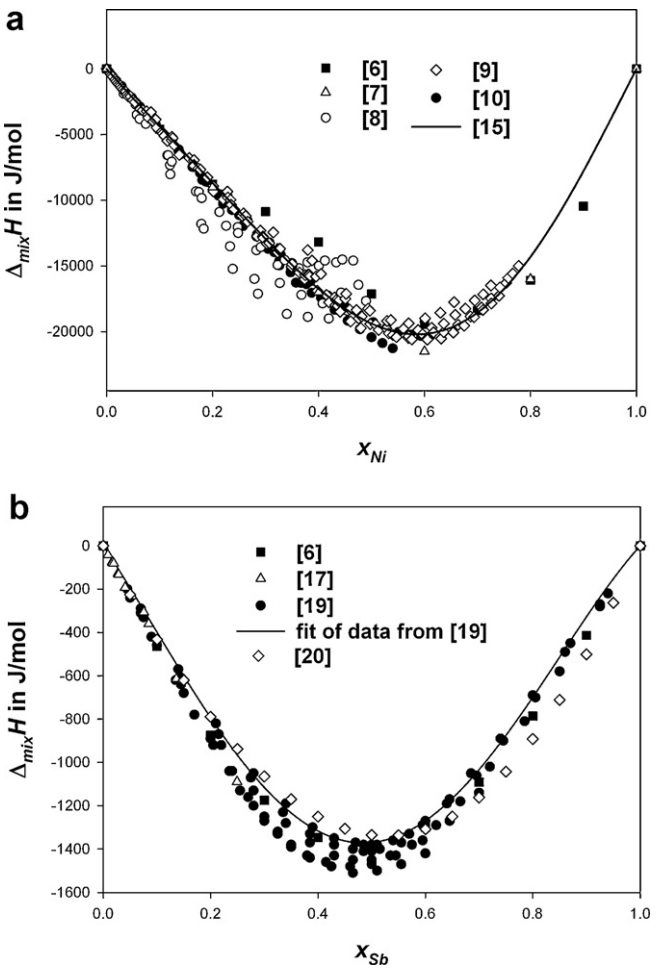

Fig. 1. (a) Literature information to the enthalpy of mixing of liquid Ni–Sn alloys. (b) Literature information to the enthalpy of mixing of liquid Sb–Sn alloys.

formation refer to solid alloys and compounds. Considering the rather high enthalpy of formation of solid Ni–Sb compounds the enthalpy of mixing should be less exotherm.

2.2. The Ni–Sn binary system

The partial and integral enthalpy of mixing as well as limiting partial enthalpy of Ni in Sn has been investigated several times by calorimetric methods. The results published until 1970 are compiled in Hultgren et al. [6]. Later on, further measurements have been published by Pool et al. at 1307 °C [7], by Luck et al. [8] at 1502, 1429, and at 1387 °C and in the range of 594–1306 °C by Haddad et al. [9]. Recently Flandorfer et al. [10] has measured the partial and integral enthalpy of mixing at 1100, 1250 and 1500 °C using drop calorimetry methods. No significant temperature dependence of $\Delta_{mix}H$ could be observed within this temperature range. Thermodynamic assessments for the binary system were published by Nash et al. [11], Ghosh [12], Miettinen [13], and Liu et al. [14]. Very recently Glibin et al. [15] have calculated the enthalpy of mixing of liquid Ni–Sn alloys at 1307 °C and compared their results with some experimental data. Generally, a good agreement with experimental data was obtained. A comparison of the experimental literature data including the calculated values given by Glibin et al. [15] is shown in Fig. 1a. The results of Pool et al. [7], Haddad et al. [9], Flandorfer et al. [10] and Glibin et al. [15] agree very well. The data of Luck et al. [8] are in the same range but scatter much more. The kink towards less exothermic values at $0.2 \le x_{Ni} \le 0.6$ reported in Hultgren's compilation [6] could not be reproduced by any of the experimental investigations.

2.3. The Sb–Sn binary system:

Several calorimetric investigations of the enthalpy of mixing of liquid Sb–Sn alloys can be found in the literature. In 1930, Kawakami [16] was the first to measure it at 800 °C. Later the binary system was investigated by Kleppa [17] at 450 °C, and Wittig and Gehring [18] at 700 °C. All these data have been incorporated to the compilation of Hultgren et al. [6]. Later Sommer et al. [19] determined the enthalpy of mixing of liquid alloys in the temperature range from 510 °C to 835 °C, and Azzaoui et al. [20] at 619 °C ($0.5 \le x_{Sn} \le 1$) and at 640 °C ($0 \le x_{Sn} \le 0.5$) to conclude finally that all the experimental results agree to satisfaction. A small but significant temperature dependence of $\Delta_{mix}H$ and the formation of two associates, SbSn and $SbSn_2$, was postulated by Sommer et al. [19].

EMF methods were applied to derive the corresponding $\Delta_{mix}H$ values by Frantik and Mcdonald [21] and Vassiliev et al. [22]. Very recently Chen et al. [23] described the liquid phase in the Sb–Sn system using a regular solution model assuming temperature independent heat of mixing. The calculated values are in good agreement with the experimental data reported by Wittig et al. [18], Sommer et al. [19] and Azzaoui et al. [20]. A comparison of the experimental literature data including calculated values based on a least square fit of data given by Sommer et al. [19] for 835 °C is shown in Fig. 1b

2.4. The Ni–Sb–Sn ternary system

To the best knowledge of the authors no data for the enthalpy of mixing of liquid alloys in the Ni–Sb–Sn ternary system are available from literature.

3. Experimental procedure

The calorimetric measurements were carried out in a Calvet-type twin calorimeter with two thermopiles with more than 200 thermocouples each, wire wound resistance furnace, and an automatic drop device for up to 30 drops. Control and data evaluation was performed using LabView and HiQ software as described by Flandorfer et al. [24]. To prevent oxidation all measurements were conducted under Ar flow (99.999% Ar, approx. 30 ml/min). At the end of each series the calorimeter was calibrated by five drops (between 30 and 50 mg each) of NIST standard α-Al_2O_3 (National Institute of Standards and Technology, Gaithersburg, MD).

The samples were prepared from nickel wire (99.99%), tin rod (99.99%), and antimony shots (99.999%). Antimony was further purified by filtering the liquid metal under vacuum through quartz glass wool. Samples of pure metals (Ni, Sb, or Sn) at ambient temperature were dropped into a bath of Sb or binary alloy Sb–Sn, Ni–Sn or Ni–Sb, respectively, of chosen starting composition at furnace temperature of 1000 °C. All measurements were carried out using a graphite crucible ($\varnothing_i$ = 9 mm, height = 90 mm) which was heated at 1000 °C for 10 min before using it to remove surface impurities.

The enthalpy of mixing was determined for Ni–Sb and for the following composition cross-sections in the ternary: x_{Sb}/x_{Sn} = 3:1, x_{Sb}/x_{Sn} = 1:1, x_{Sb}/x_{Sn} = 1:3, x_{Ni}/x_{Sn} = 1:4, and x_{Ni}/x_{Sb} = 1:4 at 1000 °C.

The interval time between individual drops was usually 40 min and the heat flow acquisition interval was ~0.5 s. Obtained signals were recorded, integrated and quantified applying the calorimeter constant evaluated by calibration. The measured enthalpy (integrated heat flow at constant pressure) is:

$$\Delta H_{drop} = n_i.[H_{i(l),FT} - H_{i(s),DT}] + \Delta H_{reaction} \quad (1)$$

Table 1
Binary and ternary interaction parameters in Ni–Sb–Sn.

System	Reference	Interaction Parameters (J/mol)
Ni–Sb	This work	$^0L = -92{,}215$ $^1L = -42{,}187$
Ni–Sn	[10]	$^0L = -78{,}327$ $^1L = -36{,}751$
Sb–Sn	[19]	$^0L = -5477$ $^1L = 488$ $^2L = 2265$
Ni–Sb–Sn	This work	$^0M = 179{,}673$ $^1M = 19{,}609$ $^2M = 31{,}215$

where n_i is the number of moles of the dropped element i, FT = furnace temp., and DT = drop temperature. $H_{i(l),FT} - H_{i(s),DT}$ was calculated using the polynomials for the thermodynamic data of pure elements in the SGTE data base [25]; SGTE Unary Database version v5.0 – 2 June 2009. For the respective temperatures FT and DT, the average of the values for each drop of a run was taken because their scattering was low enough do not influence the accuracy of the method. Because of the rather small masses added, the partial enthalpy $\Delta_{mix}\bar{H}_i$ can be considered as:

$$\Delta_{mix}\bar{H}_i \approx \frac{\Delta H_{reaction}}{n_i} \quad (2)$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of substance:

$$\Delta_{mix}H = \sum_i \frac{\Delta H_{reaction;i}}{n_{crucible} + \sum_i n_{drop;i}} \quad (3)$$

The respective binary starting value for the sections in the ternary system was calculated from the information listed in Table 1.

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and "chemical errors", e.g. incomplete reactions or impurities. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than ±1% for the HT-1000. The systematic errors are mainly caused by parasitic heat flows, base line problems at signal integration and dropping and mixing problems. One can estimate that the overall error is ±250 J/mol.

4. Results and discussion

4.1. Experimental results

Because of the lack of literature data for Ni–Sb measurements have been performed by dropping pure solid Ni into liquid Sb at 1000 °C. The results can be seen in Table 2a and Fig. 2. The total mass loss of Sb was close to 12%. Under the assumption that only Sb has evaporated, the mass loss was introduced into our calculations. A least square fit according to the well-known Redlich–Kister polynomial [26] and an extrapolation to pure Ni resulted in the curve shown in Fig. 2. There is a general exothermic behavior with a minimum at approx. 55 at.% Ni and −24,500 J/mol. In addition, we have calculated $\Delta_{mix}H$ at 0 K from the ΔG^E data given in the assessment of Zhang et al. [3] for Ni–Sb. Considering that no experimental $\Delta_{mix}H$ data have been available for the assessment the agreement is highly satisfying. Our data fit has been used to calculate the binary starting values for the respective ternary section E; see Fig. 3. For Ni–Sn (section D) we calculated the binary data from Flandorfer et al. [10] because these data have been determined under same conditions in our laboratory and well agree with most of literature values. The experimental data of Sommer et al. [19] have been chosen in order to determine the binary $\Delta_{mix}H$ values for Sb–Sn (sections A–C). This work appeared to be very comprehensive and well discussed. Moreover, there is a good agreement with most of the literature data.

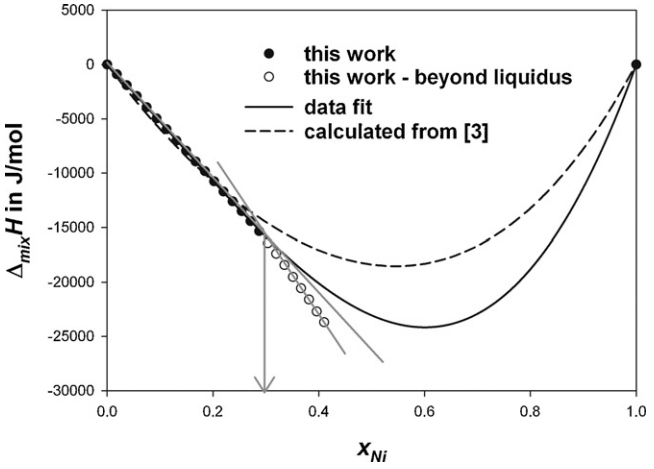

Fig. 2. Integral molar enthalpies of mixing of liquid Ni–Sb alloys at 1000 °C; standard states: pure liquid metals.

The experimental data for the investigated sections (see Fig. 3) in the systems Ni–Sb–Sn are collected in Table 2b. This Table contains all the necessary information like calibration factor k, starting amounts, added amounts, and the corresponding heat effects, as well as the calculated partial and integral enthalpies of mixing of the liquid alloys.

The course of the integral enthalpies of mixing along section A (pure Ni dropped into liquid $Sb_{0.74}Sn_{0.26}$) is shown in Fig. 4a. It starts at a slightly exothermic value in the Sb–Sn binary and quickly becomes more negative. The extrapolation of the experimental values (see chapter 3.2) leads to a minimum of approx. −20,000 J/mol at $x_{Ni} = 0.54$. The other two sections starting from $Sb_{0.5}Sn_{0.5}$ and $Sb_{025}Sn_{0.75}$, respectively, show a very similar behavior where the minimum is slightly shifted to higher Ni contents; see Fig. 4b. This reflects the quite similar mixing behavior of Sb and Sn with Ni. The minima between 55 and 59 at.% Ni indicates the compound forming tendency leading to the respective most stable intermetallics NiSb and Ni_3Sn_2 in the two binary systems. Both compounds exhibit the AsNi structure type and a significant homogeneity range.

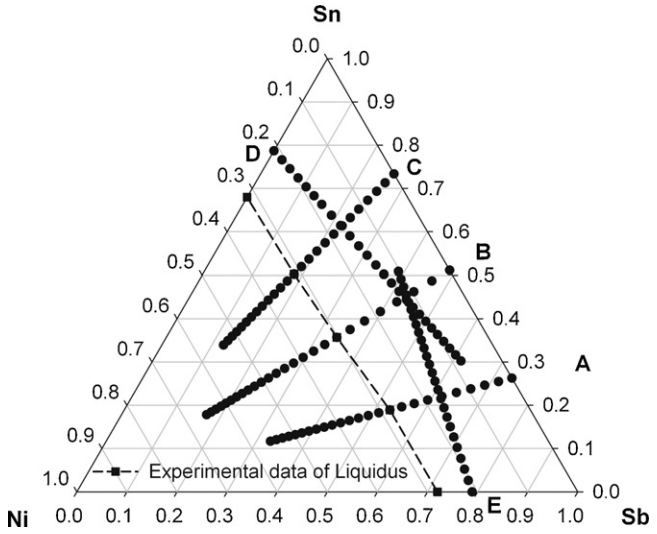

Fig. 3. Measured sections (A, B, . . .E) and alloy compositions in the ternary Ni–Sb–Sn system at 1000 °C (intersections indicated according to Tables 2a and 2b); the estimated liquidus limit is marked by the dashed line.

Table 2a
Partial and integral molar enthalpies of mixing of liquid Ni–Sb alloys at 1000 °C; standard states: pure liquid metals.

Dropped mole	Drop enthalpy	Partial enthalpy		Integral enthalpy*	
n(Ni) [mmol]	ΔH_{drop} [J]	x(Ni)**	$\Delta_{mix}\bar{H}_{ni}$ [J/mol]	x(Ni)	$\Delta_{mix}H$ [J/mol]
Starting amount: n(Sb) = 22.4903 mmol, calibration: 5 pieces NIST-sapphire, k = 0.7927 ± 0.0020 J/(μV s)					
0.4204	−2273	0.0092	−52759	0.0183	−968
0.4457	−2677	0.0277	−53359	0.0371	−1906
0.4614	−2836	0.0465	−53499	0.0559	−2911
0.4783	−3345	0.0653	−54345	0.0747	−3933
0.5039	−3685	0.0842	−54665	0.0937	−4975
0.5095	−3102	0.1029	−53440	0.1122	−5965
0.5368	−4593	0.1216	−55909	0.1309	−7019
0.5444	−2119	0.1401	−51245	0.1492	−7950
0.5614	−3717	0.1583	−53973	0.1673	−8930
0.5657	−2169	0.1761	−51187	0.1849	−9821
0.5824	−3753	0.1936	−53796	0.2022	−10757
0.6171	−3727	0.2111	−53392	0.2199	−11700
0.6319	−3425	0.2285	−52772	0.2372	−12612
0.6488	−3404	0.2457	−52598	0.2543	−13506
0.6659	−4809	0.2626	−54574	0.2710	−14429
0.6795	−5433	0.2792	−55348	0.2874	−15349
0.7032	−10594	0.2956	−62417	0.3037	−16419
0.7197	−8455	0.3117	−59099	0.3196	−17393
0.7369	−11360	0.3274	−62769	0.3352	−18429
0.7717	−13099	0.3432	−64326	0.3512	−19525
0.7902	−12841	0.3589	−63603	0.3666	−20561
0.8119	−13769	0.3741	−64311	0.3816	−21594
0.8173	−18137	0.3888	−69544	0.3961	−22709
0.8389	−14592	0.4032	−64747	0.4103	−23693

* Per mole of binary mixture.
** Average of x_{Ni} before and after the drop.

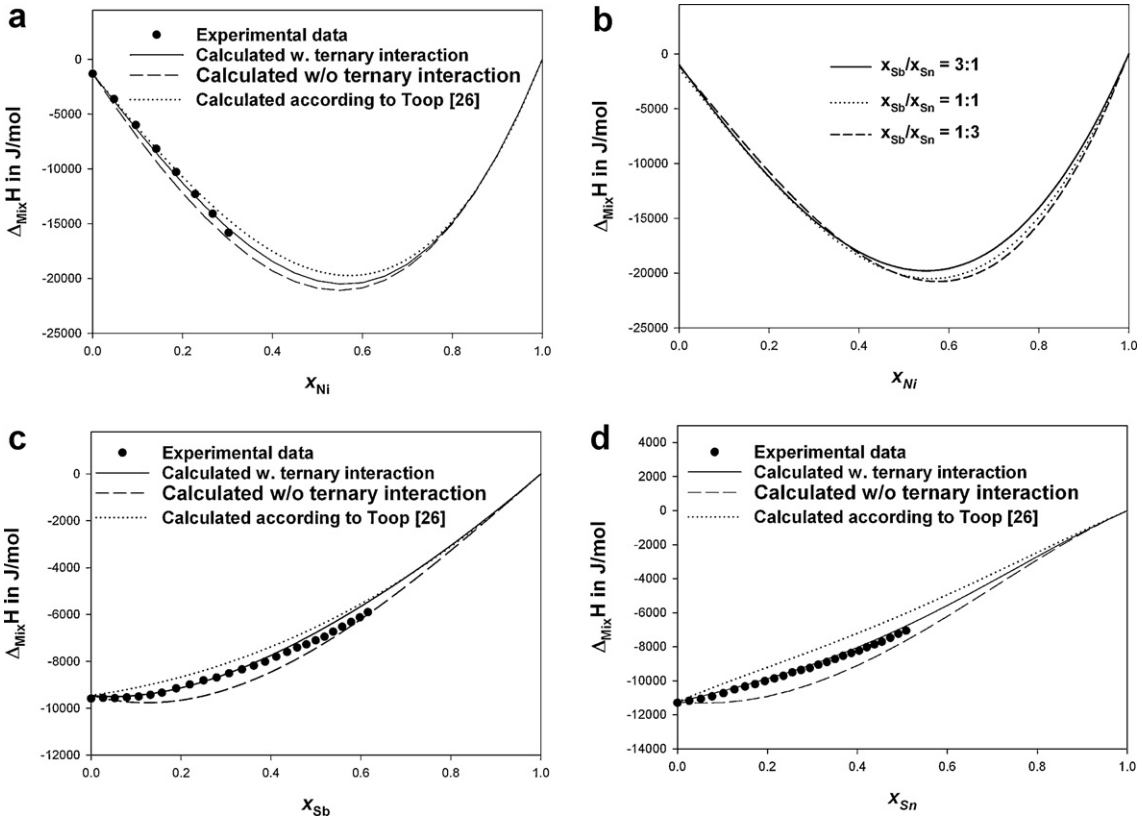

Fig. 4. (a) Integral molar enthalpies of mixing of liquid Ni–Sb–Sn alloys at 1000 °C for the section x_{Sb}/x_{Sn} = 3:1; standard states: pure liquid metals. (b) Integral molar enthalpies of mixing of liquid Ni–Sb–Sn alloys at 1000 °C for the sections x_{Sb}/x_{Sn} = 3:1, 1:1 and 1:3; standard states: pure liquid metals. (c) Integral molar enthalpies of mixing of liquid Ni–Sb–Sn alloys at 1000 °C for the section x_{Ni}/x_{Sn} = 1:4; standard states: pure liquid metals. (d) Integral molar enthalpies of mixing of liquid Ni–Sb–Sn alloys at 1000 °C for the section x_{Ni}/x_{Sb} = 1:4; standards states: pure liquid metals.

Table 2b
Partial and integral enthalpies of mixing of liquid Ni–Sb–Sn alloys, 1000 °C; standard states: liquid pure components.

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_i [mmol]	ΔH_{Drop} [J]	x_i^*	$\Delta_{mix}\bar{H}_i$ [J/mol]	x_{Ni}	x_{Sb}	$\Delta_{mix}H$ [J/mol]
Section A: x_{Sb}/x_{Sn} = 3:1; i = Ni; starting amounts: n_{Sb} = 8.1283 mmol; n_{Sn} = 3.0208 mmol, calibration: 5 pieces of NIST-sapphire, k = 0.6097 ± 35 J/(μV s)						
0.0000	–	0	–	0	0.7291	−944
0.3510	−4943	0.0153	−52318	0.0305	0.7068	−2512
0.3899	−4768	0.0464	−52144	0.0623	0.6836	−4140
0.4210	−4815	0.0783	−52191	0.0944	0.6602	−5783
0.4620	−4666	0.1108	−52041	0.1271	0.6364	−7456
0.5046	−4204	0.1437	−51579	0.1603	0.6122	−9133
0.5380	−4125	0.1767	−51501	0.1930	0.5883	−10783
0.5476	−3353	0.2084	−50729	0.2238	0.5659	−12306
0.5522	−2405	0.2381	−49780	0.2525	0.5450	−13693
0.5613	−4177	0.2661	−51553	0.2796	0.5252	−15066
0.5687	−14913	0.2924	−62288	0.3052	0.5066	−16740
0.5740	−9515	0.3172	−56890	0.3292	0.4891	−18127
0.5770	−18704	0.3404	−66080	0.3517	0.4727	−19736
0.5783	−20265	0.3622	−67640	0.3728	0.4573	−21294
0.5853	−7001	0.3828	−54376	0.3928	0.4427	−22349
0.6058	−10537	0.4025	−57912	0.4122	0.4286	−23485
0.6088	−7515	0.4213	−54891	0.4304	0.4152	−24462
0.6424	−8544	0.4395	−55919	0.4485	0.4020	−25461
0.6454	−4128	0.4571	−51504	0.4656	0.3896	−26267
0.6475	−1364	0.4736	−48739	0.4817	0.3779	−26943
0.6541	−1128	0.4893	−48503	0.4970	0.3667	−27580
Section B: x_{Sb}/x_{Sn} = 1:1; i = Ni; starting amounts: n_{Sb} = 3.6994 mmol; n_{Sn} = 3.8718 mmol, calibration: 5 pieces of NIST-sapphire, k = 0.6201 ± 35 J/(μV s)						
0	–	0	–	0	0.4886	−1371
0.3785	−2344	0.0238	−49719	0.0476	0.4654	−3673
0.4253	−2865	0.0718	−50240	0.0960	0.4417	−6038
0.4452	−1726	0.1188	−49102	0.1416	0.4194	−8212
0.4765	−2131	0.1636	−49507	0.1856	0.3979	−10328
0.5125	−1207	0.2069	−48582	0.2282	0.3771	−12327
0.5177	−782	0.2475	−48157	0.2669	0.3582	−14123
0.5262	−2503	0.2846	−49878	0.3024	0.3409	−15857
0.5305	4	0.3186	−47372	0.3349	0.3250	−17325
0.5356	−4398	0.3498	−51773	0.3648	0.3104	−18873
0.5495	−9678	0.3788	−57054	0.3928	0.2967	−20556
0.5539	−1627	0.4057	−49002	0.4186	0.2841	−21765
0.5615	10212	0.4306	−37163	0.4426	0.2723	−22402
0.5624	221	0.4537	−47154	0.4648	0.2615	−23386
0.5716	−890	0.4752	−48266	0.4856	0.2514	−24352
0.5821	6361	0.4954	−41014	0.5052	0.2418	−24986
0.5836	5308	0.5142	−42068	0.5233	0.2329	−25614
0.5856	6609	0.5318	−40767	0.5403	0.2246	−26152
0.5913	11586	0.5482	−35790	0.5562	0.2168	−26486
0.6023	20815	0.5638	−26560	0.5713	0.2094	−26489
0.6177	19391	0.5786	−27985	0.5858	0.2024	−26540
0.6329	24265	0.5928	−23110	0.5997	0.1956	−26425
0.6592	30156	0.6064	−17219	0.6132	0.1890	−26115
0.7070	30880	0.6199	−16496	0.6267	0.1824	−25779
0.7154	30758	0.6330	−16618	0.6394	0.1762	−25467
0.7398	31147	0.6455	−16229	0.6517	0.1702	−25153
Section C: x_{Sb}/x_{Sn} = 1:3; i = Ni; starting amounts: n_{Sb} = 3.0178 mmol; n_{Sn} = 8.3060 mmol, calibration: 5 pieces of NIST-sapphire, k = 0.6128 ± 97 J/(μV s)						
0	–	0	–	0	0.2665	−1019
0.3241	−1330	0.0139	−48705	0.0278	0.2591	−2346
0.3295	−1980	0.0412	−49355	0.0546	0.2520	−3639
0.3692	−1502	0.0687	−48877	0.0828	0.2444	−4991
0.3905	−1541	0.0969	−48916	0.1110	0.2369	−6338
0.3965	−1084	0.1244	−48459	0.1378	0.2298	−7609
0.4045	−567	0.1507	−47942	0.1636	0.2229	−8815
0.4377	−541	0.1767	−47916	0.1897	0.2159	−10039
0.4854	−731	0.2033	−48107	0.2169	0.2087	−11317
0.4999	−382	0.2300	−47758	0.2431	0.2017	−12535
0.5092	−443	0.2556	−47818	0.2680	0.1951	−13696
0.5216	2158	0.2800	−45217	0.2919	0.1887	−14724
0.5338	7324	0.3033	−40051	0.3148	0.1826	−15542
0.5353	8372	0.3255	−39004	0.3363	0.1769	−16278
0.5632	14012	0.3469	−33364	0.3575	0.1712	−16824
0.5645	7644	0.3675	−39731	0.3774	0.1659	−17535
0.5706	12459	0.3869	−34916	0.3964	0.1609	−18064
0.5957	11723	0.4056	−35652	0.4149	0.1559	−18605
0.6032	11677	0.4238	−35698	0.4326	0.1512	−19122
0.6033	12071	0.4409	−35304	0.4493	0.1468	−19597
0.6181	12677	0.4573	−34699	0.4653	0.1425	−20037
0.6284	12183	0.4730	−35193	0.4807	0.1384	−20474
0.6424	13147	0.4882	−34228	0.4956	0.1344	−20868
0.6504	13513	0.5027	−33862	0.5098	0.1306	−21233

Table 2b (*Continued*)

Mole dropped	Drop enthalpy	Partial enthalpy		Integral enthalpy		
n_i [mmol]	ΔH_{Drop} [J]	x_i*	$\Delta_{mix}\bar{H}_i$ [J/mol]	x_{Ni}	x_{Sb}	$\Delta_{mix}H$ [J/mol]
0.6701	16954	0.5167	−30421	0.5236	0.1270	−21492
0.7097	21073	0.5305	−26303	0.5374	0.1233	−21632
Section D: x_{Ni}/x_{Sn} = 1:4; i = Sb; starting amounts: n_{Ni} = 1.8363 mmol; n_{Sn} = 6.7864 mmol, calibration: 5 pieces of NIST-sapphire, k = 0.6287 ± 44 J/(μV s)						
0	–	0	–	0.2130	0	−9592
0.2363	39790	0.0133	−8335	0.2073	0.0267	−9558
0.2432	38146	0.0397	−9978	0.2017	0.0527	−9570
0.2658	39545	0.0661	−8580	0.1960	0.0796	−9542
0.2760	40024	0.0927	−8100	0.1904	0.1059	−9500
0.2913	40939	0.1190	−7186	0.1848	0.1321	−9432
0.2998	41799	0.1448	−6325	0.1794	0.1575	−9341
0.4016	43708	0.1735	−4416	0.1726	0.1894	−9156
0.4105	43452	0.2044	−4672	0.1662	0.2195	−8989
0.4503	43629	0.2348	−4495	0.1597	0.2500	−8813
0.4675	42471	0.2647	−5653	0.1535	0.2793	−8689
0.4748	44065	0.2931	−4059	0.1476	0.3068	−8513
0.5365	43687	0.3212	−4437	0.1415	0.3355	−8344
0.5387	43777	0.3488	−4347	0.1359	0.3620	−8185
0.5535	44316	0.3745	−3808	0.1305	0.3871	−8013
0.5921	45363	0.3995	−2761	0.1253	0.4119	−7801
0.6260	45191	0.4239	−2933	0.1201	0.4359	−7601
0.6295	45369	0.4471	−2756	0.1154	0.4582	−7410
0.6326	44205	0.4686	−3919	0.1110	0.4790	−7276
0.6832	45130	0.4893	−2994	0.1066	0.4996	−7106
0.7047	45000	0.5094	−3124	0.1024	0.5193	−6950
0.7405	46603	0.5288	−1521	0.0983	0.5383	−6735
0.8573	46116	0.5485	−2008	0.0940	0.5586	−6527
0.9244	46129	0.5686	−1995	0.0898	0.5785	−6323
0.9818	46166	0.5882	−1958	0.0856	0.5978	−6123
0.9976	46955	0.6068	−1169	0.0818	0.6157	−5902
Section E: x_{Ni}/x_{Sb} = 1:4; i = Sn; starting amounts: n_{Ni} = 1.7516 mmol; n_{Sb} = 6.5539 mmol, calibration: 5 pieces of NIST-sapphire, k = 0.6294 ± 81 J/(μV s)						
0	–	0	–	0.2109	0.7891	−11287
0.2241	27826	0.0131	−7165	0.2054	0.7684	−11179
0.2328	28244	0.0392	−6746	0.1999	0.7480	−11061
0.2363	29557	0.0646	−5433	0.1946	0.7283	−10913
0.2544	31162	0.0897	−3829	0.1893	0.7083	−10718
0.2567	32159	0.1145	−2832	0.1842	0.6892	−10505
0.2643	30891	0.1384	−4100	0.1792	0.6705	−10332
0.2655	29768	0.1615	−5223	0.1745	0.6528	−10197
0.2688	31683	0.1835	−3308	0.1699	0.6358	−10017
0.2766	30934	0.2048	−4057	0.1655	0.6192	−9862
0.2820	31068	0.2255	−3923	0.1612	0.6031	−9708
0.2900	33185	0.2456	−1806	0.1570	0.5874	−9502
0.2971	30894	0.2652	−4097	0.1529	0.5722	−9362
0.3165	29909	0.2846	−5082	0.1488	0.5568	−9247
0.3229	32922	0.3038	−2069	0.1448	0.5419	−9055
0.3426	31740	0.3227	−3251	0.1408	0.5270	−8895
0.3461	32629	0.3412	−2362	0.1370	0.5127	−8718
0.3656	32669	0.3593	−2322	0.1332	0.4985	−8541
0.3906	32473	0.3774	−2518	0.1294	0.4841	−8367
0.4009	31475	0.3953	−3516	0.1257	0.4702	−8227
0.4099	33803	0.4127	−1188	0.1221	0.4567	−8026
0.4237	32767	0.4295	−2224	0.1186	0.4436	−7860
0.4544	32462	0.4462	−2529	0.1150	0.4304	−7701
0.5369	33965	0.4639	−1026	0.1111	0.4157	−7473
0.5542	34494	0.4821	−496	0.1073	0.4016	−7236
0.5769	33087	0.4997	−1904	0.1037	0.3879	−7054

* Average value before and after the drop.

The formation of a solid phase during dropping of Ni to liquid Sb–Sn alloys was clearly indicated by a jump of the partial enthalpies and a corresponding kink in the integral enthalpy curve. Accordingly, the points on the 1000 °C liquidus isotherm derived for the three ternary sections have been added to the Gibbs triangle shown in Fig. 3.

Section D (pure Sb dropped into liquid $Ni_{0.21}Sn_{0.78}$), and section E (pure Sn dropped into liquid $Ni_{0.2}Sn_{0.8}$) are shown in Fig. 4c and d, respectively. Enthalpy curves start at rather strong exothermic values in the binary systems Ni–Sn or Ni–Sb and become less negative towards Sb–Sn. For both sections the alloy in the crucible has been fully liquid throughout the entire run; see also Fig. 3. In Table 3, the integral enthalpy values from the both respective sections (see Fig. 3) at the cross sections a, b, c, d and e are compared. The agreement is generally very good; the maximum deviation of 300 J/mol is within the random error of ±250 J/mol. Thus we can exclude a serious systematic error by the method we used.

4.2. Ternary modeling

The experimental results were described by a least square fit to the Redlich–Kister–Muggianu polynomial which is given by the

Table 3
Estimated experimental values of the integral enthalpy of mixing at the intersection points a, b, c, d and e.

Intersection	Integral enthalpy of mixing [J/mol]		
	Ni drops	Sb drops	Sn drops
a(A,E)	−9700		−10,000
b(D,E)		−7600	−7850
c(B,E)	−7400		−7700
d(B,D)	−7400	−7600	
e(C,D)	−9200	−9100	

following equation:

$$\Delta_{\mathrm{mix}}H = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\nu} {}^{\nu}L^{H}_{i,j}\left(x_i - x_j\right)^{\nu}\right] + x_i x_j x_k \left({}^{(0)}M^{H}_{i,j,k}x_i + {}^{(1)}M^{H}_{i,j,k}x_j + {}^{(2)}M^{H}_{i,j,k}x_k\right) \quad (4)$$

where i, j, k are equal to 1, 2, 3 for the element Ni, Sb and Sn respectively. The binary parameters ${}^{\nu}L_{i,j}$ ($\nu = 0,1,2\ldots$) were determined from literature as given in Table 1. The excess ternary interaction parameters ${}^{\alpha}M_{i,j,k}$ ($\alpha = 1$, 2 and 3) were obtained from the experimental enthalpies of mixing of the present work. The results for the ternary interaction parameters ${}^{\alpha}M_{i,j,k}$ ($\alpha = 1$, 2 and 3) are as well shown in Table 1. They are generally positive and thus effect a shift to less exothermic values compared to the pure extrapolation of binary data according to Muggianu.

Finally the above equation was used to calculate the enthalpy of mixing of liquid Ni–Sb–Sn at 1000 °C for the entire composition range. The result is presented as an iso-enthalpy plot which is shown in Fig. 5. It is noteworthy that the data outside of the fully liquid region at 1000 °C (shaded field) have to be considered as extrapolated values for metastable liquid alloys. The integral enthalpy of mixing for the entire ternary system is exothermic and becomes less negative with decreasing Ni-content.

The course of $\Delta_{\mathrm{mix}}H$ along the measured sections A, B, C, D and E was calculated with and without ternary interaction (see Eq. (4)) and added to Fig. 4a, c, and d for sections A, D, and E. It can be seen that in case of sections D (Sb drops) and E (Sn drops) there is a significant deviation to the experimental values without ternary interactions. However, it does not necessarily mean that a real ternary interaction takes place in the liquid mixture. More likely the extrapolation model according to Muggianu is not the best choice for this system. The fact having two very similar constituents (Ni–Sb and Ni–Sn) and the much less exothermic Sb–Sn as the third one implies that the asymmetric Toop model [27] could be more suitable. Therefore $\Delta_{\mathrm{mix}}H$ according to the extrapolation model of Toop was additionally plotted in Fig. 4a, c, and d. Generally, the values are less exothermic compared to the Muggianu model. In case of sections D and E they fit to the experimental values slightly better but not as good as the values calculated with ternary interactions. Interestingly, Grytsiv et al. [28] reported the occurrence of a real ternary compound in the Ni–Sb–Sn system at ~25 at.% Ni and 42–58 at.% Sb. However, it exists only at temperatures lower than 500 °C and does not melt congruently. Overall, a ternary interaction for the formation of the liquid Ni–Sb–Sn cannot be deduced from our data.

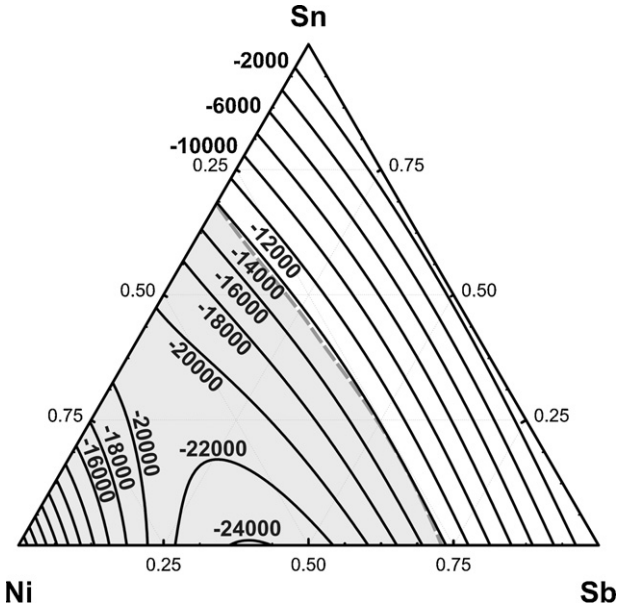

Fig. 5. Isoenthalpy curves of liquid Ni–Sb–Sn alloys at 1000 °C; standard states: pure liquid metals; metastable liquid region is indicated by shadowed field.

5. Conclusion

Based on very accurate and reproducible experimental data gained by drop calorimetry along five cross sections the enthalpy of mixing of liquid Ni–Sb–Sn alloys could be described. Additionally, we present the first experimental data for the enthalpy of mixing of liquid Ni–Sb alloys. The enthalpy values at the intersections of the cross sections show only rather small deviations. Thus we can conclude that our method is reliable and the binary starting values are consistent. Our data will be helpful to improve thermodynamic optimizations of the liquid phase of the Ni–Sb–Sn system which is important for several technical applications, e.g. lead-free soldering.

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